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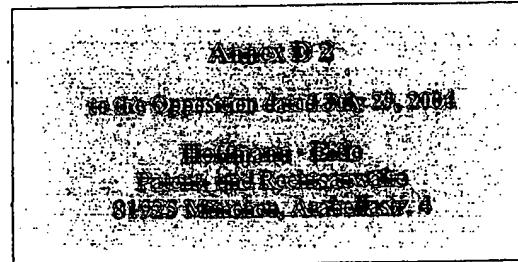
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⑮ 発明の名称 超微粒子の製造方法

⑯ 特 願 昭58-225363

⑰ 出 願 昭58(1983)12月1日

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3 発明の詳細な説明

明細書

1 発明の名称

超微粒子の製造方法

2 特許請求の範囲

1. ハロゲン化ニオブとナトリウムを気相で反応させることによる超微粒子ニオブの製造方法。
2. 反応を、副生するハロゲン化ナトリウムの沸点以下の温度でおこなう特許請求の範囲第一項記載の方法。
3. ハロゲン化ニオブを反応室に高濃度で導入する特許請求の範囲第一項、第二項記載の方法。
4. ハロゲン化ニオブを1m/秒以上の線速度で反応室に導入する特許請求の範囲第三項記載の方法。

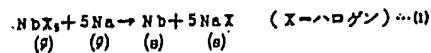
本発明はハロゲン化ニオブとナトリウム（以下「本」という）を気相で反応させ、金属ニオブの超微粒子を効率よく製造する方法に関するものである。ここで云う超微粒子粉とは粒径1μ以下の粉体をいう。超微粉体は、その微細さゆえその性質はバルク状態とはまったく異なり新しい用途が期待されている。

金属超微粉の製造方法は物理的方法としてはアトマイズ法やガス中蒸発法が、化学的方法としては熱分解法やガス還元法、気相反応法が知られている。気相反応は金属塩化物等の蒸気をH₂、CO等により還元して微粉体を得る方法で、この方法は逐段操業が可能な反面H₂、COの還元力が弱く、超微粉化し得る対象物質が限定される欠点があつた。又この方法は反応温度も比較的高温にする必要があつた。

またガス蒸発法では、蒸気圧の低い高融点金属（Nb、Ta、Mo、Wなど）では超微粒子の製造自体をわめて困難であった。

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一般に気相反応法で超微粒子をうるためには、高い過飽和度比(実際の蒸気圧/平衡蒸気圧)を実現して核生成速度を早めることが必要である。本発明でのハロゲン化ニオブとナトリウムとの還元反応は次式で示される



気相反応で生成物はすべて固体である。従って温度領域が広いため高い過飽和度比が安定してえられ、又強い還元力を有し、比較的蒸気圧の高いNaを使用するため反応速度も早い。

また反応器の構造、反応ガスの導入方法、加熱方法などの装置因子も超微粒子製造のための大きな因子である。

本発明者らは、これらを勘案して効率よくニオブの超微粒子を得る方法をもとめて研究した結果本発明を完成したものである。

次に本発明を詳述する。ハロゲン化ニオブとNaを各々不活性ガス中で気化させ、反応温度に維持してある反応室に、はじめにNa蒸気を次いでハロ

ゲン化ニオブを早い速度で送り込む。ここで用いるハロゲン化ニオブとしては塩化ニオブ(以下NbCl₅といふ)、臭化ニオブ(以下NbBr₅といふ)、汎化ニオブ(以下NbI₅といふ)、沸化ニオブ(以下NbF₅といふ)およびこれらの低級ハロゲン化物いずれをもちいても粒径1μ以下の金属ニオブがえられる。

次に本発明につきNbCl₅を用いた例をもとに更に詳述する。NbCl₅とNaの量比は(1)式に示したごとくモル比で1:5が当量であり、本発明においても当量であれば事実上よいが好ましくは0.5~2.0当量、さらに好ましくは0.8~1.2当量の範囲で反応させることが望ましい。なぜなら0.8当量より小ではNbCl₅の損失が大きくなり、1.2当量より大では不経済であるばかりか過剰のNa処理が繁雑となるからである。

反応は300°C以上で開始するので、反応温度は300°C以上あればよく、上限温度は核生成速度を早くするため副生するNaClの沸点1400°C以下であることが好ましく、特に好ま

しくはその融点の800°C以下である。前記融点以下で反応させることにより、粒径が均一な粒子がえられる。

気化したNbCl₅は融点以上の温度に保ち、あらかじめNa蒸気が導びかれている反応室内に高速で送り込むことが好ましい。

反応室へ吹き出す速度は超微粉の微生物を得る上で高精度で導入することがよく、1m/sec以上であれば特に限定されないが反応室の長さの制限から3m/sec以下が望ましい。

反応は通常大気圧でおこなわれるが装置面から許されるならば減圧下もしくは加圧下でおこなうこと也可能である。

生成した超微粉のニオブ、副生するNaClおよび過剰のNaの捕集するときの温度条件は特に限定されないが、100°C以上に保ち捕集しながらNaを分離しても0°C以下に冷却して捕集してもよい。

捕集した生成物は水を含まない有機溶剤を用いてNaおよびNaClを除去することが簡便である。洗浄後有機溶剤の付着している超微粒子は50°C

以下の限度を含む不活性ガス中もしくは乾燥空気中で乾燥することにより、超微粒子の表面に酸化膜を生成させ安定化させることができる。

本発明によれば高収率で0.5~0.2μmの金属ニオブがえられる。

又、比較的低温での瞬間的な反応であるため、きわめて効率よく生成できる。

更に還元剤のナトリウムも比較的安価なので經濟性にすぐれている。

次に実施例で本発明を更に詳述する。

実施例1

市販のフェロニオブを塩素化して常法により不純物を除去してえた純度99.9%のNbCl₅600gをNbCl₅ホッパーに込んだ。

市販Naを気化器で760°Cに保ち11L/minのArガスをキャリヤーとしてNa蒸気(Na 5g/min)を800°Cに保った縦型の反応室上部より導入した。一方、NbCl₅はホッパーからスクリューまで300°Cに保った気化室に10g/minで送り気化

させ、 NaCl_4 を1 L/min のArで反応室内にノズルをとうして1 m/sec の線速度をもって導入した。

Naの割合は NaCl_4 の1.2倍当量であった。

反応室下部の出口から捕集器に導びかれたNb超微粉、ナトリウムおよび塩化ナトリウムの混合物は反応終了後捕集器ごと反応器からはずしてエチルアルコール1 μ を加えNaを溶解させ沈降分離でエチルアルコールを除去した。ここでえられたスラリーにエチレングリコール9 μ を加え NaOH を溶解させ、沈降分離でニオブ超微粉を分離エチルアルコールで洗浄した。

エチルアルコール中の超微粉スラリーは、室温の乾燥空気中でエチルアルコールを気化させ超微粉の表面を酸化安定化した。

えられた超微粉ニオブは次の様であった。

| | |
|----|------------------|
| 収量 | 180 g (収率 87%) |
| 粒度 | 0.05 ~ 0.1 μ |
| Nb | 94.4% |
| O | 5.6% |
| Br | 0.1% |

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超微粒子ニオブの電子顕微鏡写真($\times 50000$)
を図1に示した。

実施例2

実施例1で使用した装置を用いて NbBr_5 とNaを反応させた。

NbBr_5 を0.3 g/minの割合で気化させノズルより反応室にふきこんだ。同時にNa蒸気を2 g/minの割合で600°Cに保った反応室に通した。キャリヤーとしてのArガスは各々2 L/min , 1.5 L/min であった。

生成した超微粉は2アミノエタノール1.5 μ , エタノール3 μ を使用してNaおよび NaBr を除去するとともに安定化した。

| | | |
|----|-----------|-----|
| 収率 | 90% | 85% |
| Nb | 92% | |
| O | 8% | |
| Br | n.d. | |
| 粒径 | 0.2 μ | |

図2にえられた超微粉の電子顕微鏡写真($\times 100000$)

を示した。

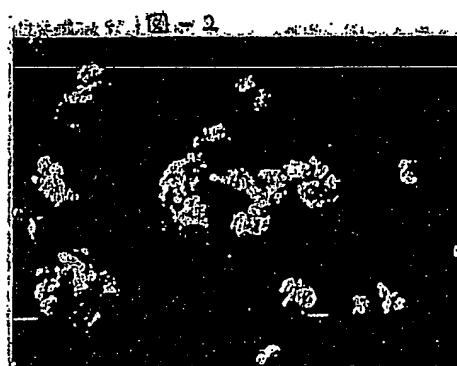
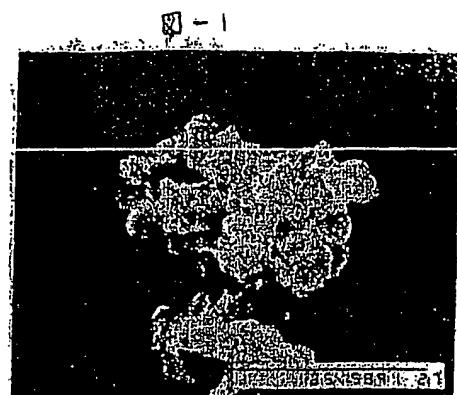
4 図面の簡単な説明

図1は NbCl_4 とNaの反応でえられた超微粒子の電子顕微鏡写真($\times 50000$)

図2は NbBr_5 とNaの反応でえられた超微粒子の電子顕微鏡写真($\times 100000$)である。

特許出願人 東洋電機工業株式会社

特開昭60-121207(4)



TRANSLATION

Unexamined Published Japanese Patent Application
No. S60-121207

Title of the Invention:

Process for Producing Ultrafine Particles

Publication Date: June 28, 1985

Patent Application No. S58-225363

Filing Date: December 1, 1983

Applicant: Tosoh Corporation

Inventor: H. Sudo, I. Hirano and K. Nishizawa

1. TITLE OF THE INVENTION

Process for Producing Ultrafine Particles

2. CLAIMS

1. A process for producing ultrafine particulate niobium, comprising reacting a niobium halide with sodium in a gaseous phase.

2. The process as claimed in claim 1, wherein the reaction is performed at a temperature not higher than the boiling point of sodium halide which is generated as a by-product.

3. The process as claimed in claim 1 or 2, wherein the niobium halide is introduced into a reaction chamber at a high linear velocity.

4. The process as claimed in claim 3, wherein the niobium halide is introduced into a reaction chamber at a linear velocity of at least 1 m/sec.

3. DETAILED DESCRIPTION OF THE INVENTION

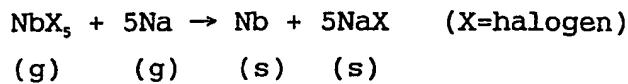
The present invention relates to a process for efficiently producing ultrafine particles of metal niobium by reacting a niobium halide with sodium (hereinafter referred to as "Na") in a gaseous phase. The term "ultrafine particle powder" as used herein means a powder having a particle size of 1 μm or less. Owing to the fineness, ultrafine powder materials

exhibit properties utterly different from those in the bulk state and are expected to bring new uses.

With respect to the process for producing metal ultrafine powder, physical processes such as atomization and evaporation in gas, and chemical processes such as thermal decomposition, gas reduction and gas phase reaction are known. The gas phase reaction is a process of reducing a vapor of a metal chloride or the like by H₂, CO or the like to obtain a fine particle material. According to this process, a continuous operation can be performed, however, the objective material which can be formed into ultrafine powder is disadvantageously limited because H₂ or CO is weak in the reducing power. Furthermore, this process requires a relatively high reaction temperature.

According to the gas evaporation process, in the case of a high melting point metal (e.g., Nb, Ta, Mo, W) having a low vapor pressure, the production itself of ultrafine particles is very difficult.

In general, for obtaining ultrafine particles by a gas phase reaction, it is necessary to realize a high oversaturation degree ratio (i.e., actual vapor pressure/equilibrium steam pressure) and thereby elevate the nucleation rate. The reducing reaction between a niobium halide and sodium in the present invention proceeds as shown in the following scheme (1):



In the gas phase reaction, all products are obtained as solid. Therefore, the temperature region is broad and a high oversaturation degree ratio can be stably obtained. Furthermore, since Na used has a strong reducing power and a relatively low vapor pressure, the reaction proceeds at a high rate.

In addition, the structure of reactor, the method of introducing the reaction gas, the heating method and other structural factors are also important factors in the production of ultrafine particles.

By taking account of these, the present inventors have

made studies for a method of efficiently obtaining ultrafine particulate niobium, as a result, they have accomplished the present invention.

The present invention will be described in detail below. A niobium halide and Na each is vaporized in an inert gas. Thereafter, Na steam and then a niobium halide are fed at a high linear velocity into a reaction chamber maintained at a reaction temperature. The niobium halide used here may be any of niobium chloride (hereinafter referred to as "NbCl₅"), niobium bromide (hereinafter referred to as "NbBr₅"), niobium iodide (hereinafter referred to as "NbI₅"), niobium fluoride (hereinafter referred to as "NbF₅") and lower halides thereof. Whichever is used, a metal niobium having a particle size of 1 μ m or less can be obtained.

In the following, the present invention is described in detail by specifically referring to the case where NbCl₅ is used. With respect to the ratio between NbCl₅ and Na, the equivalent is, as shown in scheme (1), 1:5 in terms of a molar ratio. In the present invention, it may be sufficient in practice if the ratio is equivalent, however, the reaction is preferably performed at a ratio of from 0.5 to 2.0 equivalent, more preferably from 0.8 to 1.2 equivalent. If the ratio is less than 0.8 equivalent, the loss of NbCl₅ increases, whereas if it exceeds 1.2 equivalent, not only this is unprofitable but also a cumbersome treatment for excess Na is necessary.

The reaction starts at 300°C or higher, therefore, the reaction temperature is suitably 300°C or higher and in order to increase the nucleation rate, the upper limit of the temperature is preferably not higher than the boiling point of NaCl, namely, 1,400°C or lower, more preferably not higher than the melting point thereof, namely, 800°C or lower. When the reaction is carried out at a temperature not higher than the melting point, particles having a uniform size can be obtained.

The vaporized NbCl₅ is preferably kept at a temperature not lower than the dew point and fed at a high speed into a reaction chamber where Na steam is previously introduced.

With respect to the speed in blowing the gas into the reaction chamber, the gas is preferably introduced at a high linear speed so as to obtain an ultrafine product. The blowing speed is not particularly limited as long as it is 1 m/sec or more, however, in view of the limited length of the reaction chamber, the blowing speed is preferably 3 m/sec or less.

The reaction is usually performed under atmospheric pressure, however, if the equipment allows, the reaction may be performed under reduced or increased pressure.

At the time of collecting the produced ultrafine niobium powder, the by-product NaCl and the excessive Na, the temperature condition is not particularly limited and Na may be separated while collecting those by keeping the temperature at 100°C or higher, or those may be cooled to 0°C or lower and then collected.

From the products collected, Na and NaCl can be easily removed using an organic solvent not containing water. After the rinsing, the ultrafine particle having attached thereto the organic solvent is dried in an inert gas or dry air containing oxygen at 50°C or lower to form an oxide film on the surface of the ultrafine particle, so that the ultrafine particle can be stabilized.

According to the present invention, metal niobium of a particle diameter of from 0.05 to 0.2 μm can be obtained in a high yield.

Furthermore, this is an instantaneous reaction occurring at a relatively low temperature, therefore, the production can be attained with extremely high efficiency.

In addition, sodium as a reducing agent is relatively inexpensive, therefore, the production cost is low.

The present invention is described in greater detail below by referring to the following Examples.

Example 1

600 g of NbCl₅ having a purity of 99.9% which was obtained by chlorinating a commercially available ferroniobium and removing impurities in a usual manner, was charged into an

NbCl₅ hopper.

A commercially available Na was kept at 760°C in a vaporizer and the Na vapor (Na: 5 g/min) was introduced from the upper portion of a vertical reaction chamber kept at 800°C using 11 λ/min of Ar gas as a carrier gas. On the other hand, NbCl₅ was fed from the hopper to a vaporizing chamber kept at 300°C at 10 g/min by means of a screw. The NbCl₅ was then introduced into the reaction chamber through a nozzle at a linear velocity of 1 m/sec using 1 λ/min of Ar.

The ratio of Na was 1.2 times equivalent to NbCl₅. A mixture of Nb ultrafine powder, sodium and sodium chloride was guided from the outlet at the lower portion of the reaction chamber to a collector and after the completion of reaction, the collector as a whole was taken off from the reactor. To the mixture, 1 λ of ethyl alcohol was added to dissolve Na and the ethyl alcohol was removed by sedimentation. To the resulting slurry, 9 λ of ethylene glycol was added to dissolve NaCl and the niobium ultrafine powder was separated by sedimentation and washed with ethyl alcohol.

The ultrafine powder slurry in the ethyl alcohol was stabilized by vaporizing the ethyl alcohol in dry air at room temperature and thereby oxidizing the ultrafine powder surface.

The thus-obtained ultrafine niobium had the following results:

| | |
|--------------------|--------------------|
| Yield: | 180 g (yield: 87%) |
| Particle diameter: | 0.05 to 0.1 μm |
| Nb: | 94.4% |
| O: | 5.6% |
| Cl: | 0.1% |

Fig. 1 is an electron microphotograph (×50,000) of the ultrafine particulate niobium.

Example 2

Using the apparatus used in Example 1, NbBr₅ and Na were reacted with each other.

More specifically, NbBr₅ was vaporized at a rate of 8.3 g/min and blown into a reaction chamber through a nozzle. At

the same time, Na vapor passed through the reaction chamber kept at 600°C, at a rate of 2 g/min. In these, Ar gas as a carrier was used at a rate of 2 λ /min and 1.5 λ /min, respectively.

Using 1.5 liter of 2-aminoethanol and 3 liter of ethanol, Na and NaBr were removed and at the same time, the ultrafine powder produced was stabilized.

| | |
|--------------------|-------------|
| Yield: | 90%, 85 g |
| Nb: | 92% |
| O: | 8% |
| Br: | n.d. |
| Particle diameter: | 0.2 μ m |

FIG. 1 is an electron microphotograph ($\times 10,000$) of the ultrafine particulate niobium obtained.

4. BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is an electron microphotograph ($\times 50,000$) of ultrafine particles obtained by a reaction between NbCl_5 and Na.

FIG. 2 is an electron microphotograph ($\times 10,000$) of ultrafine particles obtained by a reaction between NbBr_5 and Na.



FIG. 1

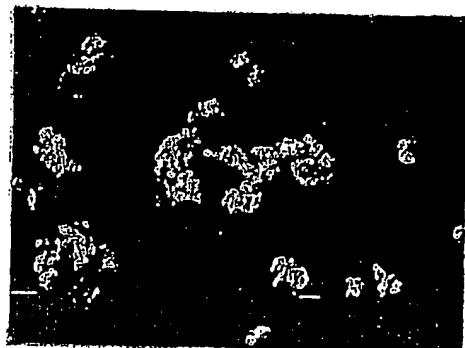


FIG. 2

DECLARATION

Re: European Patent No. 0 946 323

I, Masako Kimura of 3-6, Namiki 7-chome, Abiko-shi, Chiba 270-1165 Japan, do solemnly and sincerely declare that I understand the Japanese language and the English language well, and that the attached English version is a true, accurate and faithful partial translation made by me of:

Unexamined Published Japanese Patent Application
No. S60-121207

I make this solemn declaration conscientiously believing the same to be true.

This ninth day of July, 2004


Masako Kimura

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